

Multi-Atom Resonant Photoemission in Cr/Fe Bilayers and Alloys: Sensing Lengths and Compositional Clustering

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INTRODUCTION

Although many existing experimental techniques can provide information on the elements present in a given sample of material, as well as on their local structural and bonding environment and their magnetic properties, we lack a broadly applicable probe which can determine whether a given type of atom is actually located in close physical proximity to another type of atom. Multi-atom resonant photoemission (MARPE), an effect recently discovered at the ALS in experiments on beamline 9.3.2, appears to provide such a probe [1]. This effect makes use of the well-known specificity of core electron excitation energies to each element, but takes this specificity one step further by involving two atoms at once. When the energy of the exciting x-rays is tuned through a core absorption edge of one atom the excitation strength is found to be transferred to a neighboring atom via an interatomic resonant process, with increases of up to 100% in the resulting photoelectron intensity being observed. The effect was first seen in photoelectron emission from various metal oxides [1], and it has by now also been observed in the secondary decay processes of Auger emission and soft x-ray emission [2], thus expanding its range of applicability.

Although preliminary accounts of the theory of this effect have been presented [1, 3], these have to date not provided a quantitative assessment of the sensing length of the phenomenon, i.e. the distance up to which resonating atoms can contribute significantly to the intensity enhancement. In order to estimate the sensing lengths of MARPE, we have thus studied the dependence of the Cr $2p$ intensity enhancement induced at the Fe L_3 edge in Cr/Fe bilayers of varying Cr and Fe layer thicknesses, as well as in $\text{Cr}_x\text{Fe}_{1-x}$ alloy thin films of varying composition. The resulting data also suggest compositional clustering in the alloy films, pointing to a general future application of the effect.

EXPERIMENTAL

Photoemission experiments and partial electron yield measurements of the x-ray absorption coefficient were performed on bending-magnet beamline 9.3.2 of the ALS. Cr/Fe bilayer films were prepared by vapor deposition of Fe and then Cr at a rate of about 1 monolayer per minute and a pressure of $1\text{--}2\cdot 10^{-10}$ torr onto a clean W(110) substrate at near 300 K. $\text{Cr}_x\text{Fe}_{1-x}$ alloy films 150 Å thick and with the Cr concentration, x , in the range from 7% to 100% were grown on W(110) under similar conditions by varying the relative Cr and Fe deposition rates to achieve the desired alloy composition. Deposition rates were determined with a quartz microbalance and checked before and after deposition. Cr and Fe layer thicknesses, as well as alloy compositions, were confirmed after deposition using quantitative angle-dependent photoelectron spectroscopy and x-ray absorption spectroscopy. No indications of surface segregation of Cr or Fe were found in the alloy films.

RESULTS

The Cr $2p$ intensity was found to be enhanced by up to 85% upon sweeping the x-ray energy through the Fe $2p$ absorption edges, as shown in Fig. 1(a) for a thin Cr overlayer on thick Fe,

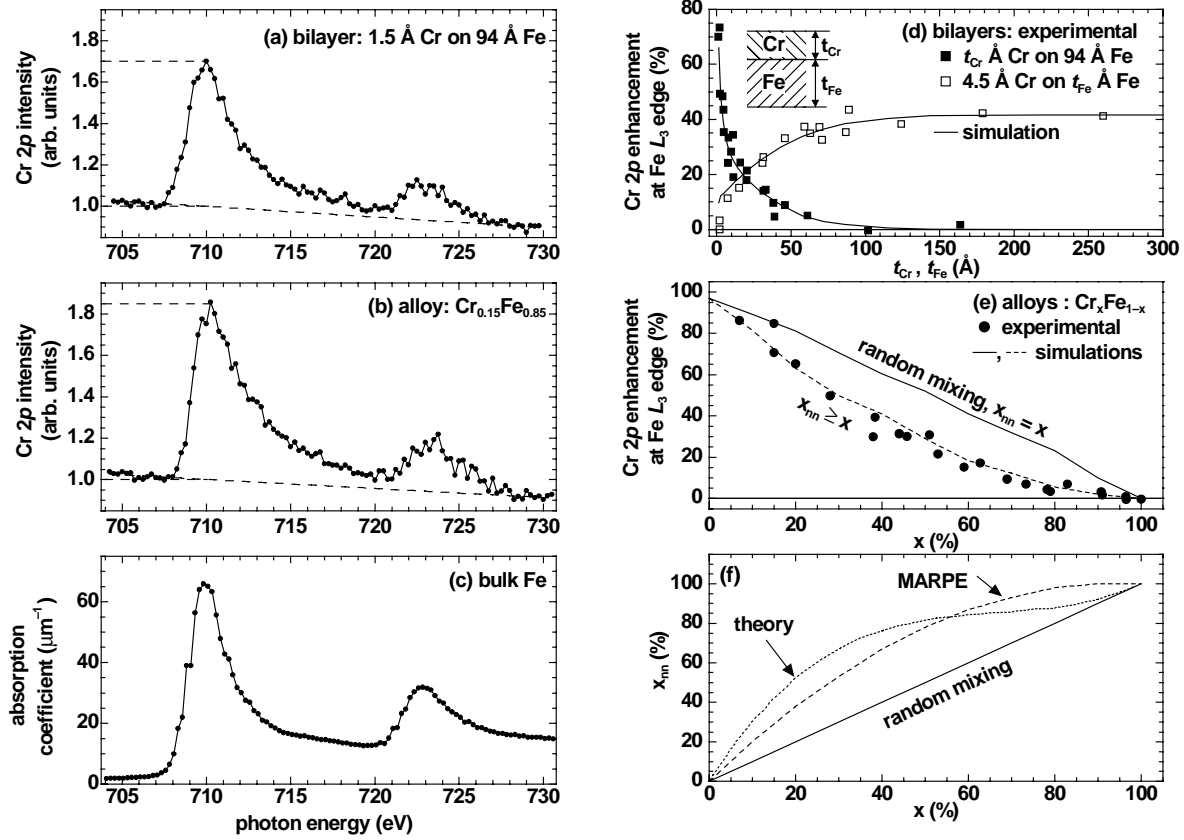


Figure 1. Multi-atom resonant photoemission (MARPE) and x-ray absorption results for Cr/Fe bilayers and alloys. (a) Cr 2*p* photoemission intensity for a thin 1.5 Å Cr layer on 94 Å Fe as photon energy is scanned through the Fe *L*_{3,2} edges. The dashed line indicates the expected Cr 2*p* intensity without interatomic excitations. (b) As (a), but for an iron-rich Cr_{0.15}Fe_{0.85} alloy. (c) X-ray absorption coefficient for Fe at the Fe *L*_{3,2} absorption edges. (d) MARPE enhancement of the Cr 2*p* photoemission intensity at the Fe *L*₃ edge for Cr/Fe bilayers with iron thickness *t*_{Fe}=94 Å and varying Cr thickness *t*_{Cr} (solid squares) and *t*_{Cr}=4.5 Å and varying *t*_{Fe} (open squares). The solid curves are empirical fits to this data involving enhanced near-neighbor contributions. (e) MARPE enhancement of the Cr 2*p* intensity at the Fe *L*₃ edge for Cr_xFe_{1-x} alloys of varying composition *x*. The experimental results are displayed as solid circles. Simulations of the data based on random mixing in the alloy (solid curve) and with empirically derived near-neighbor Cr compositional clustering via the parameter *x*_{nn} (dashed curve) are also shown. (f) Near-neighbor Cr composition *x*_{nn} as a function of alloy composition *x*: solid straight line = random mixing, dashed curve = experimental, as derived from our MARPE results, dotted curve = independent theoretical prediction [4].

and in Fig. 1(b) for an Fe-rich alloy, with both MARPE enhancements closely following the Fe 2*p* x-ray absorption coefficient shown in Fig. 1(c), a similarity noted in previous experiments [1, 2]. These data have been obtained over a broad range of Cr and Fe thicknesses, as well as alloy compositions, with the resulting intensity enhancements summarized in Figs. 1(d) and 1(e). The solid curves in these panels represent the best fit to the data with an empirical model in which the short-range near-neighbor contributions are much enhanced (~5000×) with respect to the long-range contributions, with the latter fitted very well by an exponential decay with decay lengths of 25-30 Å. Near neighbors within about 3 Å of the emitting atom are thus found to contribute

about half of the overall effect. However, the marked convex curvature in the alloy data of Fig. 1(e) can only be described if we introduce compositional clustering in the alloy, with Cr preferring to have Cr near neighbors (dashed curve). This results in the near-neighbor composition x_{nn} shown in Fig. 1(f) (dashed curve), an experimental determination of this quantity. The extent of short-range compositional clustering in this system has also been calculated theoretically according to the first correlation approximation of the free-energy inverse-temperature expansion method [4]. These results [dotted curve in Fig. 1 (f)] are compared with the experimental short-range Cr concentration derived from MARPE in Fig. 1(e), and the agreement is quite good. These results thus better quantify the interaction range of MARPE, provide a first application of it to compositional clustering in alloys, and together with other work [1, 2] point to the broad future utility of this measurement for studying various types of heterogeneity in alloys and complex materials, as well as at surfaces and buried interfaces.

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